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Large Scale Carbon Dioxide Release: Short-Cut Analytical Modelling and Application

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The ongoing development of CCS applications and installations at large scale involves the need of improving the knowledge of connected hazards resulting from accidental loss of containments, or intentional events. In fact, a massive release of CO_2 can have catastrophic consequences for humans: the processes determining the hazards posed by accidental releases of CO_2 from pressurized systems are complex, due to the thermodynamics of the outflow, with changes of phase, followed by the dispersion of the cold heavy gas. In this paper, we explore a peculiar scenario connected to a massive release of carbon dioxide and following accumulation driven by negative buoyancy effect under semi confined conditions, either due to low wind and natural complex orography, or to the presence of geometrical complications. The paper sets out a preliminary analytical model, developed under simplifying but conservative hypotheses, which can be conveniently adopted at least at the early stage of the evaluation process or for establishing emergency procedures defining critical distances and possible man exposure to the hazardous dose.

1. Introduction

Effective modelling of CO2 release situation is essential for pipeline and storage design and safe operation within sensitive or inhabited areas, as well as in obtaining stakeholder acceptance. In the aftermath of severe accidents Regulatory Bodies, research companies, healthy organizations and more generally society are forced to re-examine the way things were done, determine immediate and root causes and make appropriate changes possibly applying novel methodologies and solutions (Vairo et al., 2016). Case histories provide an empirical contribution to our understanding on the hazard distances for CCS projects, also in view of QRA based decision. A well-known accident involving a massive and sudden release triggered by a natural event took place in Cameroon where carbon dioxide accumulated over the years in the lower strata of Nyos lake, was released with low momentum for a total estimated mass of 1.5 million tonnes (Kling et al., 1986). The natural orography of the valley with a flat depression allowed accumulation and transport, causing nearly 1700 fatalities and a large number of killed livestocks. A previous example is provided by the extreme outburst of carbon dioxide occurred in 1953 in Menzengraben evaporate (potash) mine (former East Germany). Under still wind and stable weather conditions an estimated mass of 1100-3900 tonnes gave rise to a high momentum vertical release, with little impingement, and the subsequent CO2 accumulation caused several fatalities and injured people by asphyxiation (Hedlund, 2012). Different theoretical studies focused on simulating the release and dispersion of dense phase CO2 from high-pressure media (Witlox et al., 2009) using CFD and hazard analysis software tools (e.g. Dixon et al., 2012). Moreover recent experimental studies still under development are addressed at experimentally verify all relevant physical aspects in order to develop and validate mathematical models for discharge and dispersion from dense-phase CO2 pipelines (Jamois et al., 2014) and connected loss of containment frequency (Milazzo et al., 2015), or storage sites. For instance, the Shell Barendrecht carbon dioxide sequestration project foresees that the compressed gas would be stored in an empty natural gas cavity beneath the town of Barendrecht (NL). In this case, although in the Netherlands an individual risk criterion of 10^{-6} at contours around a static risk source is well established, the QRA-based decision was overruled. However, when conservative results are enough as a first screening tool, analytical

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models can be conveniently applied in hazard assessment (Fabiano et al., 2015), to evaluate hazardous maximum build-up (Palazzi et al., 2013), or to evaluate hazardous events posing a higher risk than the safety level and to determine safety measures (Abrahamsen et al., 2013). The objective of the current work is to develop a short-cut model for predicting on the basis of few parameters, the scale and extent of the hazardous area for the most sensitive receivers, without accounting on CFD models needing proper accurate set-up and long computational time (e.g. Basso et al., 2015).

2. Modelling framework

Figures 1 a-b-c describe the simplified time evolution of a quasi-instantaneous carbon dioxide release, under still wind conditions. A dense cloud of volume V_0, having similar vertical dimension, h_0, and horizontal dimension, $2\ r_0$, near the source is formed, it is subject to slumping by gravity and it is diluted with air as it expands radially. After a rapid initial dilution, completing the sublimation phase of carbon dioxide, the initial momentum of the release is exhausted, because of its higher than air density and its friction with the ground. Schematically, the dense cloud slumps under the influence of gravity while increasing its radius, r, and reducing its height, h.

The evaluation of the total mass of the cloud, after the jet phase and at the beginning of the slumping phase, m_0, is performed by assuming the proportionality between the mass of entrained air and the initial release momentum flux. The subsequent spreading neglects the influence of atmospheric turbulence and wind, as a first simplified approach and relies on the non-dimensional density definition introduced by van Ulden (1974).

Under the assumptions of flat terrain, no obstructions, no local concentration fluctuation, no chemical reaction, the unsteady – state behaviour of a nearly instantaneous carbon dioxide release, near the ground, can be described by following Eqs (1)-(4):

$$\frac{dV}{dt} = k\pi r^2 v_r \tag{1}$$

$$v_r = \frac{dr}{dt} \tag{2}$$

$$v_r = \frac{1}{r}\sqrt{\frac{\rho_0 - \rho_a}{\rho_0}\, g \frac{V_0}{\pi}} \tag{3}$$

$$V = \pi r^2 h \tag{4}$$

Eqs (1)-(4), allow determining the characteristics of the cloud depending on the horizontal dimension, r, and/or time ,t, once given the value of the mass release at the end of the jet phase, m_r,

By combining Eq (1), which defines the air entrainment speed within the cloud and Eq (2), providing the cloud slumping speed, with subsequent integration one can write:

$$V = V_0 + \frac{1}{3}k\pi(r^3 - r_0^3) \cong V_0 + \frac{1}{3}k\pi r^3 \tag{5}$$

Starting from similar studies (Webber, 2011), we considered the following 4 reference operative situations for storage/transport (respectively I-IV), namely: Ti= 273 K and pi = 100 bar; Ti= 273 K and pi = 200 bar; Ti= 323 K and pi = 100 bar; Ti= 323 K and pi = 200 bar. We explored the six environmental conditions schematized in in Table 1, thus obtaining 24 reference release scenarios.

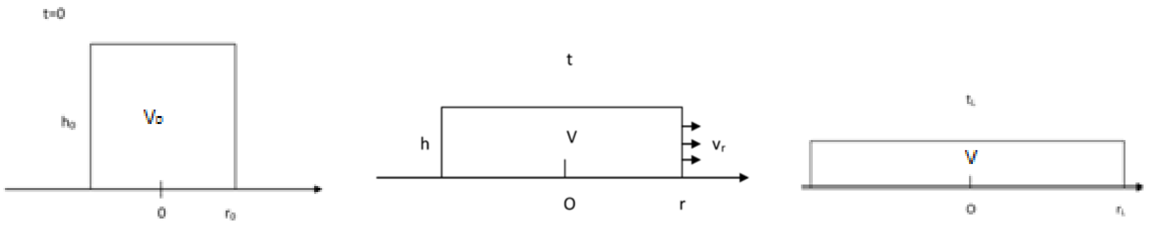

Figure 1 a-b-c : Physical model of a nearly instantaneous carbon dioxide release and time evolution.

Table 1: Explored environmental conditions

	1	**2**	**3**	**4**	**5**	**6**
T [K]	273	273	298	298	323	323
y_w	0	0.006	0	0.0313	0	0.1216

For the purposes of dose calculation, it is fundamental to determine the post release variations of carbon dioxide concentration y(r), during the cloud slumping. Starting from the jet modelling developed in Palazzi et al., 2016, it can be assumed:

$$V_0 = \frac{m_0}{\rho_0} = \frac{m_r}{\rho_0 w_0} \tag{6}$$

$$V - V_0 = \frac{m_r}{\rho_a}\left(\frac{1}{w} - \frac{1}{w_0}\right) \tag{7}$$

By combining Eqs (6) and (7), the correlation between the volume, V, and the released mass, m_r, can be obtained:

$$V = \alpha_V m_r \tag{8}$$

where the parameter α_v [$m^3\ kg^{-1}$] is provided by:

$$\alpha_V = \frac{1}{\rho_0 w_0} + \frac{1}{\rho_a}\left(\frac{1}{w} - \frac{1}{w_0}\right) \tag{9}$$

Combining Eq(5) and Eq(7):

$$r = \alpha_r m_r^{1/3} \tag{10}$$

where the parameter α_r [$m\ kg^{-1}$] is provided by:

$$\alpha_r = \left[\frac{3}{k\pi\rho_a}\left(\frac{1}{w} - \frac{1}{w_0}\right)\right]^{1/3} \tag{11}$$

From Eq(4), it follows:

$$h = \alpha_h m_r^{1/3} \tag{12}$$

where the parameter α_h [$m^3\ kg^{-1/3}$] is provided by::

$$\alpha_h = \frac{\alpha v}{\pi \alpha_r^2} \tag{13}$$

The carbon dioxide concentration during the cloud slumping, y(r), can be obtained with some straightforward calculations as follows:

$$y(r) = \left[1 + \frac{M_r}{M_a}\left(\frac{1}{w_0} - 1 + \frac{1}{3}\frac{k\pi\rho_a}{m_r}r^3\right)\right]^{-1} \tag{14}$$

The simplified description of the cloud evolution as time goes on is performed according to the framework outlined in the following. Taking into account Eq(6), Eq.(3) can be conveniently written as:

$$v_r = \frac{1}{r}\left(\frac{\rho_0 - \rho_a}{\rho_0}\frac{g}{\pi}\frac{m_r}{\rho_0 w_0}\right)^{1/2} = \frac{\beta_i}{r} m_r^{1/2} \tag{15}$$

where the parameter β_i [$kg^{-1/2}\ m^2\ s^{-1}$] is provided by:

$$\beta_i = \left[\frac{(\rho_0 - \rho_a)}{\rho_0^2}\frac{g}{\pi w_0}\right]^{1/2} \tag{16}$$

By integrating Eq.(15), one can write:

$$r^2 = r_0^2 + 2\beta_i m_r^{1/2} t \cong 2\beta_i m_r^{1/2} t \tag{17}$$

At last, from Eq(17) it is possible obtaining the function *r(t)* and, if needed*, v(t), h(t)* and *y(t).* As amply known, in order to assess the CO_2 toxicity it is necessary to calculate the exposure conditions in terms of concentration and exposure duration. Given a certain value of the critical concentration y_c, the corresponding average concentration within cloud, $y_L=\frac{y_c}{2}$, is attained at the time t_L, when, owing to slumping, the cloud extension reaches the distance r_L. In other words, we cautiously evaluate the dose, $D_{\infty L}$, considering that in each point of the circumference having radius equal to r_L, the concentration is zero when $t<t_L$; the concentration is exactly y_L at the time t_L and then it reduces down as time goes on.

$$D_{\infty L} = \int_{t_L}^{\infty} y\, dt \tag{18}$$

$$D_{\infty L} = \alpha_D m_r^{1/6} \tag{19}$$

where:

$$\alpha_D = \alpha_1 \left[\frac{1}{6} \ln \frac{(\alpha_2 + 1)^3}{\alpha_2^3 + 1} + \frac{1}{\sqrt{3}} \operatorname{arccotg} \frac{2\alpha_2 - 1}{\sqrt{3}}\right] \tag{20}$$

$$\alpha_1 = \frac{1}{\beta_i} \frac{M_a}{M_r} \left(\frac{M_a}{M_r} + \frac{1}{w_0} - 1\right)^{-1/3} \left(\frac{3}{k\pi\rho_a}\right)^{2/3} \tag{21}$$

$$\alpha_2 = \left(\frac{\frac{1}{w_L} - \frac{1}{w_0}}{\frac{M_a}{M_r} + \frac{1}{w_0} - 1}\right)^{1/3} \tag{22}$$

In order to calculate the model parameters corresponding to the critical situations, we consider that the dose corresponds to the critical one, according to the condition $D_{\infty L} = D_c$. By proper substitution respectively into Eqs (19), (10) and (17), the critical mass, m_{rL}, the critical distance, r_L, and the corresponding time, t_L, can be obtained as a function of the critical dose D_c :

$$m_{rL} = \left(\frac{D_C}{\alpha_D}\right)^6 \tag{23}$$

$$r_L = \alpha_{rL} \left(\frac{D_C}{\alpha_D}\right)^2 \tag{24}$$

$$t_L = \alpha_{tL} \left(\frac{D_C}{\alpha_D}\right)^4 \tag{25}$$

At last, by means of Eqs (8) (10) (12), we obtain the corresponding critical values as an explicit function of the release characteristics:

$$V_L = \alpha_{VL} m_{rL} \tag{26}$$

$$r_L = \alpha_{rL} m_{rL}^{1/3} \tag{27}$$

$$h_L = \alpha_{hL} m_{rL}^{1/3} \tag{28}$$

$$t_L = \alpha_{tL} m_{rL}^{1/6} \tag{29}$$

where the formulae of the parameters summarized in Tale 2 are obtained from proper application of Eqs (9), (11), (13) by setting the condition $w = w_L$.

Table 2: Model parameters appearing in Eqs (26-29)

$\boldsymbol{\alpha_{VL}}$ [m^3kg^{-1}]	$\boldsymbol{\alpha_{rL}}$ [$m\ kg^{-1/3}$]	$\boldsymbol{\alpha_{hL}}$ [$m^3kg^{-1/3}$]	$\boldsymbol{\alpha_{tL}}$ [$kg^{-1/6}s$]
$\boldsymbol{\alpha_V(w_L)}$	$\boldsymbol{\alpha_r(w_L)}$	$\boldsymbol{\alpha_h(w_L)}$	$\boldsymbol{\frac{\alpha_{rL}^2}{2\beta_i}}$

By means of the aforementioned simplifying assumptions, an analytic solution of the problem was obtained. In a more general case, for example dealing with a formal QRA procedure, or when the mechanism of gravity slumping, air entrainment and thermodynamic processes must be taken into account, a finite-difference numerical method (Reverberi et al., 2009), or a proper discretization method for solving multicomponent reacting systems (Chiarioni et al., 2006) proved to be useful tools representing a satisfactory trade-off between robustness and efficiency. Analogously, a meteorological pre-processor should be used in the subsequent diffusion modelling in order to accurately calculate the values of the meteorological parameters in the boundary-layer starting from the input meteorological data acquired on-site (Vairo et al., 2014).

3. Results and discussion

The most significant results obtained by applying the developed model under the previously mentioned conditions are summarized in Tables 3 and 4. By applying the instantaneous release model, it can be observed seen that the most unfavorable situations for the carbon dioxide dispersion, are the ones which correspond to releases with less energy and stricter environmental conditions (Table 1). Additionally, it must be remarked that the model output in terms of critical parameters widely vary passing from y_L=0.125 to higher CO_2 dilutions, thus obtaining results of scarce interest in view of practical applications.

Table 3: Modelling results Run I, at conditions T=273 K, p= 100 bar, for 3 different CO_2 limit concentrations y_L.

y_L= 0.125			y_L= 0.05			y_L= 0.02		
m_{rL} [kg]	**r_L** [m]	**t_L** [s]	**m_{rL}** [kg]	**r_L** [m]	**t_L** [s]	**m_{rL}** [kg]	**r_L** [m]	**t_L** [s]
$4.62\ 10^5$	228	26	$1.62\ 10^{10}$	13,218	475	$3.31\ 10^{11}$	52,455	1,653
$4.16\ 10^5$	221	27	$1.40\ 10^{10}$	12,765	476	$2.98\ 10^{11}$	50,627	1,654
$5.15\ 10^5$	243	26	$1.80\ 10^{10}$	14,078	475	$3.69\ 10^{11}$	55,868	1,653
$4.81\ 10^5$	238	27	$1.68\ 10^{10}$	13,765	476	$3.44\ 10^{11}$	54,593	1,654
$5.28\ 10^5$	252	26	$1.85\ 10^{10}$	14,622	475	$3.79\ 10^{11}$	58,024	1,653
$5.08\ 10^5$	250	27	$1.78\ 10^{10}$	14,430	476	$3.63\ 10^{11}$	57,232	1,654

Table 4: Modelling results at a CO_2 limit concentration y_L =0.125, corresponding to Run II (273 K; 200 bar); Run III (323 K; 100 bar); Run IV (323 K; 200 bar).

Run II			***Run III***			***Run IV***		
y_L=0.125			y_L=0.125			y_L=0.125		
m_{rL} [kg]	**r_L** [m]	**t_L** [s]	**m_{rL}** [kg]	**r_L** [m]	**t_L** [s]	**m_{rL}** [kg]	**r_L** [m]	**t_L** [s]
$7.04\ 10^5$	110	4.2	$6.83\ 10^5$	81	2.3	$6.73\ 10^5$	69	1.7
$6.52\ 10^5$	114	4.8	$6.38\ 10^5$	91	3.1	$6.27\ 10^5$	76	2.2
$8.16\ 10^5$	118	4.2	$7.93\ 10^5$	88	2.3	$7.82\ 10^5$	75	1.7
$7.80\ 10^5$	124	4.8	$7.65\ 10^5$	99	3.1	$7.51\ 10^5$	82	2.1
$8.63\ 10^5$	124	4.2	$8.39\ 10^5$	92	2.3	$8.24\ 10^5$	73	1.5
$8.44\ 10^5$	131	4.8	$8.28\ 10^5$	105	3.1	$8.14\ 10^5$	87	2.1

Four main variables are explicitly accounted for in the model: two of them are connected to inherent CO_2 toxicity hazard (y_L, D_L), while the remaining two are linked to the reference critical parameters (r_L, m_{rL}). The choice of a particular value of y_c, univocally determines y_L and D_L. In connection with any given value of y_c , two peculiar curves described by Eq.(13a) and Eq.(27) are obtained.

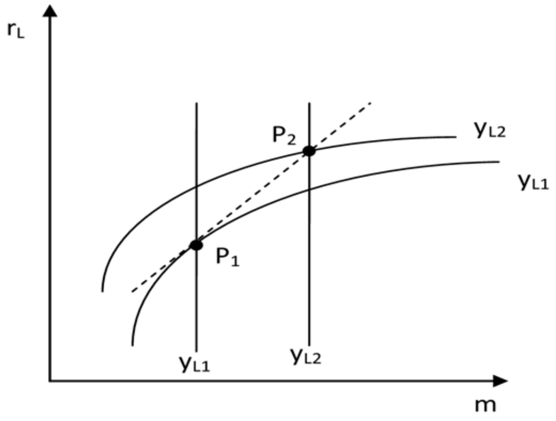

Figure 3: Graphical representation of the model, in the plane released mass versus distance.

As shown in Figure 3, the intersection of the two curves allows univocally identifying r_L and m_{rL} corresponding to y_L, as coordinates of the point P in the plan (r_L, m_{rL}). However, it should be noticed that the locus of the points of intersection of the two families of curves, at the change of y_L , will not necessarily be represented by means of an explicit equation in the form: $r_L = k\ m_{rL}^n$.

4. Conclusions

The preliminary model discussed here is straightforward to apply and the results are conservative in terms of calculating the hazardous distance and the critical mass. Under the less severe storage/transport conditions, it can be observed that the critical parameters do not depend significantly on the environmental conditions and that constantly the most unfavorable situations from the safety viewpoint are the ones corresponding to low energy releases under stricter environmental conditions. It is worth noting that the method relies on conservative simplifying assumptions, do not account for several effects, e.g. ground roughness, wind speed profile etc. In view of practical applications, the cautious results should be adopted for preliminary short-cut evaluations and emergency planning, e.g. alerting rescue teams on critical distance, critical area, man exposure and hazardous dose. A range of sensitive runs and comparison with available integral models are currently under development to determine the significance of the model uncertainty.

Reference

Abrahamsen E.B., Asche F., Milazzo M.F., 2013, An evaluation of the effects on safety of using safety standards, Safety Science 59, 173-178.

Basso D., Cravero C., Reverberi A.P., Fabiano B., 2015, CFD analysis of regenerative chambers for energy efficiency improvement in glass production plants, Energies 8, 8945-8961, DOI:10.3390/en8088945

Bonzel H.P., Bradshaw A.M., Ertl G., Eds., 1989, Physics and Chemistry of Alkali Metal Adsorption. Elsevier, Amsterdam, Nl.

Chiarioni A., Reverberi A.P., Fabiano B., Dovì V.G., 2006, An improved model of an ASR pyrolysis reactor for energy recovery. Energy 31, 2124-2132.

Dixon C., Gant S.E., Obiorah C., Biblio M., 2012, Validation of dispersion models for high pressure carbon dioxide releases. In: Hazards XXIII, Paper 21, 153–163,Southport, UK.

Fabiano B., Pistritto F., Reverberi A., Palazzi E., 2015, Ethylene–air mixtures under flowing conditions: a model-based approach to explosion conditions, Clean Techn Environ Policy 17, 1261-1270.

Hedlund F.H., 2012, The extreme dioxide outburst at the Menzengraben potash mine 7 July 1953, Safety Science 50, 537-553.

Jamois D., Proust C., Hebrard J., 2014, Hardware and instrumentation to investigate massive spills of dense phase CO_2, Chemical Engineering Transactions 36, 601-606 DOI: 10.3303/CET1436101

Kling G.W., Clark M.A., Compton H.R., Devine J.D., Evans W.C., Humphrey A.M., Koenigsberg E.J., Lockwood J.P., Tuttle M.L., Wagner G.N., 1987, The 1986 Lake Nyos Gas Disaster in Cameroon, West Africa, Science 236, 169-175.

Milazzo M.F., Vianello C., Maschio G., 2015, Uncertainties in QRA: Analysis of losses of containment from piping and implications on risk prevention and mitigation, J. Loss Prevent. Proc. Ind. 36, 98-107.

Palazzi E., Currò F., Fabiano B., 2013, Accidental continuous releases from coal processing in semi-confined environment. Energies 6(10), 5003-5022.

Palazzi E., Currò F., Lunghi E., Fabiano B., 2016, An analytical model of carbon dioxide jet from pressurized systems for safety distance evaluation, Chemical Engineering Transactions 52, in press.

Reverberi A.P., Dovì V.G., Fabiano B., Maga L., 2009, Using non-equilibrium biosorption column modelling for improved process efficiency. Journal of Cleaner Production 17, 963-968.

Vairo T., Currò F., Scarselli S., Fabiano B., 2014, Atmospheric emissions from a fossil fuel power station: dispersion modelling and experimental comparison, Chemical Engineering Transactions 36, 295-300.

Vairo T., Quagliati M., Del Giudice T., Barbucci A., Fabiano B., 2016, From land- to water-use-planning: a consequence based case-study related to cruise ship risk, Safety Science DOI: 10.1016/j.ssci.2016.03.024

Van Gelderen L., 2013, Improving a risk assessment method for CCS: public acceptance of a risk analysis for the Barendrecht project. Amsterdam: RIVMand Vrije Universiteit, Nl.

Van Ulden A.P., 1974, On the spreading of a heavy gas released near the ground, Proc. 1st Int Symp. Loss Prevention and Safety Promotion in the Process Industries, Ed. Baushmann, G., Elsevier, Amsterdam, Nl.

Witlox H.W.M., Harper M., Oke A., 2009, Modelling of discharge and atmospheric dispersion for carbon dioxide releases, J. Loss Prevent. Proc. Ind. 22,795–802.